Novel Microporous Molecular Frameworks: Potential for Gas Storage, Separation, and Catalysis

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Motivation

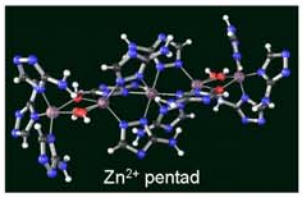
The design and synthesis of molecular-based microporous networks are areas of contemporary research activity because of their potential application for gas absorption and separation, heterogeneous catalysis, sensors, etc. The chemical tunability of the molecular components in these systems provides an additional degree of freedom not available in their inorganic zeolitic counterparts, for adjusting the pore sizes and functionality for optimal performance.

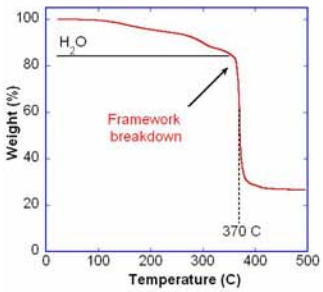
Major Achievements

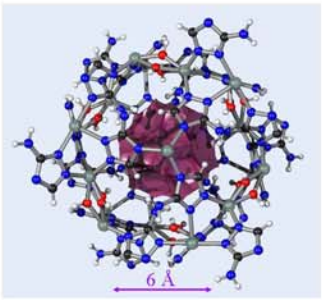
We have synthesized a series of novel complex microporous molecular frameworks based on the bridging ligand 3-amino-1,2,4-triazole (AmTAZ) containing zinc ions and auxiliary anions. A few examples are shown here:

$[Zn_5(AmTAZ)_6(OH)](NO_3)_{4/3}(OH)_{5/3}(H_2O)_x$

- Cubic assembly of pentameric rods:
  - Central Zn^{2+} octahedrally coordinated by six "inner" AmTAZ nitrogen atoms.
  - Octahedral cluster triply bridged to two tetrahedral Zn^{2+} via "inner" nitrogen atoms.
  - Disordered O/OH bridges to outermost Zn^{2+}.
  - Outermost Zn^{2+} tetrahedron is completed by coordination to outer nitrogen atoms of three AmTAZ.
- Isolated voids contain nitrate anions.
- Solvent removed below 100 °C.
- Framework stable to above 350 °C.

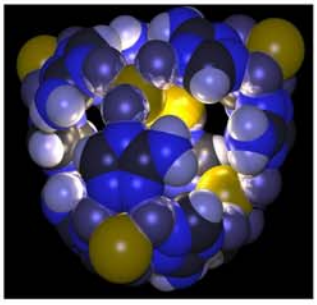


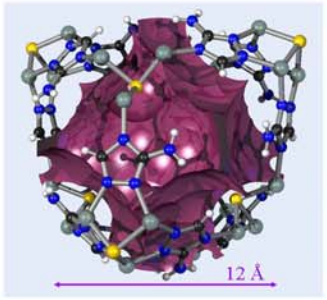




$[Zn_6(AmTAZ)_6S_2](NO_3)_3(H_3O)(H_2O)_x$

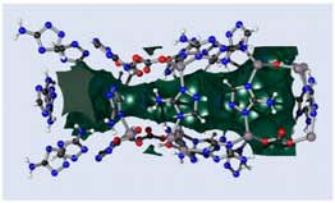
- All Zn^{2+} equivalent, tetrahedral.
- Neighboring Zn^{2+} bridged via inner nitrogen atoms of AmTAZ.
- Zn^{2+} also coordinated to outer nitrogen atom of AmTAZ of an adjacent trimer.
- Cage formed by eight trimers – four with sulfur pointing inward and four outward.
- Connected voids contain nitrate anions.



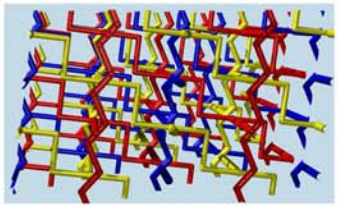


$[Zn_7(AmTAZ)_8(CO_3)_2(OH)_2](solvent)_x$

- Coordinating CO_3^{2-} anions can be used to construct *neutral* frameworks.
- Complex framework with seven unique Zn^{2+} centers.
- Three building blocks: AmTAZ-bridged trimer, carbonate-bridged dimer, and hydroxide-bridged dimer.
- An intricate, triply interpenetrated, open pore structure results.



Fragment of one pore channel.



Triply interpenetrated pore structure (schematically).

Significance

- The AmTAZ ligand has a propensity to form intricate open framework structures with zinc in the presence of auxiliary ligands.
- Carboxylate is not required for robust framework solids.
- Three-dimensional void topology is attractive for gas transport; strategically located constrictions serve as size-based separation sites
- Heteregenous local pH distribution: may promote acid-base catalytic reactions.

Future Directions

- Design of neutral frameworks so as to vacate the pores of charge compensating entities.
- The gas sorption and separation properties of these materials will be optimized.
- Combined with computational studies for detailed understanding of framework–sorbate interactions.
- Substituted and extended triazoles as well as redox-active and paramagnetic metal centers ⇒ redox-based catalysis.
- Leads to larger pores while retaining crystalline order (in comparison to other mesoporous frameworks).
- *Post facto* pore modification (e.g., atomic layer deposition, ALD)

Schlueter, J.A., Geiser, U., Funk, R. J., C. R. Chimie (in press 2006); full manuscript in preparation.

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